



# EPR spectroscopic study of Ni(I) species in the catalyst system for ethylene polymerization based on $\alpha$ -diimine Ni(II) complex activated by MMAO

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## ABSTRACT

Using EPR spectroscopy, nickel(I) species formed in the catalyst system **1**/MMAO for ethylene polymerization has been investigated (**1** = LNiBr<sub>2</sub>, L = 1,4-bis-2,4,6-dimethylphenyl-2,3-dimethyl-1,4-diazabuta-1,3-dien). It has been shown that diamagnetic cationic complex [LNi<sup>II</sup>-<sup>t</sup>Bu]<sup>+</sup>[MeMMAO]<sup>-</sup> (**2**) persists in system **1**/MMAO at low temperatures, but rapidly decays at 25 °C to give new EPR active species **3** (major product) and **4** (minor product). Species **3** is a nickel(I) complex with the proposed structure [LNi<sup>I</sup>(S)]<sup>+</sup>[MeMMAO]<sup>-</sup> (S = solvent), whereas **4** is L<sup>(\*)</sup>AlMe<sub>2</sub> species. Upon the addition of ethylene, complex **3** partially reversibly converts into the adduct [LNi<sup>I</sup>(C<sub>2</sub>H<sub>4</sub>)]<sup>+</sup>[MeMMAO]<sup>-</sup> (**5**). After ethylene consumption, species **3** restores its original concentration.

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## 1. Introduction

Today, annual production of elastomeric polyethylenes (co-polymers of ethylene with  $\alpha$ -olefins) is approaching 1 million tons. Basically, these materials are produced by ethylene copolymerization with  $\alpha$ -olefins on metallocene catalysts, which requires expensive alkylaluminum based co-catalysts [1]. The N,N- $\alpha$ -diimine-based Ni(II) catalysts, that can use aluminum alkyl chlorides as co-catalysts, are capable of producing elastomeric

polyethylenes via ethylene homopolymerization, avoiding the use of rather expensive  $\alpha$ -olefins and alkylaluminum co-catalysts [2–16]. The electronic [17–19] and steric properties [20–23] of the N,N- $\alpha$ -diimine ligands have crucial effect on the catalyst's behavior, thus providing the opportunity to finely tune the microstructure, molecular-weight distribution and hence physical properties of the synthesized polyethylene. This holds considerable promise from economic and technological perspectives. However, insufficient thermal stability of the nickel catalysts is a serious practical drawback. Currently available data on the mechanisms of ethylene polymerization by the catalyst systems based on  $\alpha$ -diimine complexes of Ni(II) are scarce, which complicates the rational design of new efficient and thermally stable catalysts.

In 2003 Brookhart and co-workers showed that cationic  $\alpha$ -diimine Ni(II) complex ([L<sub>1</sub>Ni<sup>II</sup>Me(OEt<sub>2</sub>)]<sup>+</sup>[BAR'<sub>4</sub>]<sup>-</sup> (L<sub>1</sub> = N,N-bis(2,6-diisopropylphenyl)acenaphthylene-1,2-diimine, Ar' = 3,5-C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>), obtained in the model system L<sub>1</sub>Ni<sup>II</sup>Me<sub>2</sub>/[H(OEt<sub>2</sub>)]<sup>+</sup>[BAR'<sub>4</sub>]<sup>-</sup> is capable of conducting low-temperature

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ethylene insertion into  $\text{Ni}^{\text{II}}-\text{CH}_3$  bond, yielding  $[\text{L}_1\text{Ni}^{\text{II}}-\text{Pr}]^+[\text{BAR}'_4]^-$  and  $[\text{L}_1\text{Ni}^{\text{II}}-\text{Pr}]^+[\text{BAR}'_4]^-$  species [24]. It was assumed that cationic  $\text{Ni}^{\text{II}}$ -alkyl complexes act as the active ethylene polymerization species. Possible mechanism of branched polyethylenes formation was proposed [24,25].

Recently, we have identified by  $^1\text{H}$  NMR spectroscopy cationic complexes of Ni(II), formed in real catalyst systems  $\text{LNiBr}_2/\text{MAO}$  and  $\text{LNiBr}_2/\text{MMAO}$  ( $\text{L} = 1,4\text{-bis-}2,4,6\text{-dimethylphenyl-}2,3\text{-dimethyl-}1,4\text{-diazabuta-}1,3\text{-diene}$ ,  $\text{MAO} = \text{methylalumoxane}$ ,  $\text{MMAO} = \text{Al}^i\text{Bu}_3\text{-modified methylalumoxane}$ ) [26]. Complexes  $[\text{LNi}^{\text{II}}(\mu\text{-Me})_2\text{AlMe}_2]^+[\text{MeMAO}]^-$  and  $[\text{LNi}^{\text{II}}\text{-}^t\text{Bu}]^+[\text{MeMMAO}]^-$  were observed. They were stable in reaction solutions only at low temperature (below  $-20^\circ\text{C}$ ). Further warming the samples led to the conversion of these complexes to new EPR-active paramagnetic species. Such paramagnetic compounds predominated in the reaction solution at room temperature. The structure and role of these complexes in polymerization remained unclear.

In 2015, Gao and co-workers isolated and structurally characterized a neutral Ni(I) complex  $\text{L}_1\text{Ni}^{\text{I}}(\mu\text{-Br})_2\text{AlMe}_2$  formed in the reaction of  $\text{L}_1\text{Ni}^{\text{II}}\text{Br}_2$  with  $\text{AlMe}_3$  [27]. Further addition of  $\text{AlMe}_3$  to the sample containing  $\text{L}_1\text{Ni}^{\text{I}}(\mu\text{-Br})_2\text{AlMe}_2$  lead to a new paramagnetic complex, displaying EPR spectrum characteristic of a free radical. The authors proposed that intermolecular electron transfer from Ni(I) center to the ligand affords a formally Ni(II) complex with tentative structure  $(\text{L}_1^{\bullet})\text{Ni}^{\text{II}}(\mu\text{-Br})_2\text{AlMe}_2(\text{AlMe}_3)$ . Surprisingly, both  $\text{L}_1\text{Ni}^{\text{II}}\text{Br}_2$  and  $\text{L}_1\text{Ni}^{\text{I}}(\mu\text{-Br})_2\text{AlMe}_2$  species, if activated with  $\text{AlMe}_3$ , appeared to be active in ethylene polymerization.

In 2016, Long with co-workers found that the addition of cobaltocene ( $\text{CoCp}_2$ ) to the catalyst system  $\text{L}_1\text{NiBr}_2/\text{MAO}/\text{C}_2\text{H}_4$  does not significantly affect the activity, but changes the molecular-weight characteristics and microstructure of the polyethylenes obtained [28]. This behavior was explained by reduction of the Ni center and formation of new ethylene polymerization active sites. However, the exact structure and electronic nature of these active sites is still unclear.

It was shown that cationic  $\text{Ni}^{\text{II}}$ -alkyl species can insert ethylene to form long polymeric chains, in agreement with proposed key role of these species in polymerization. However, the divalent nickel species in the catalyst systems studied are prone to reduction to monovalent state [26,29]. If nickel(I) species are inactive in ethylene polymerization, it is difficult to explain the high activity of  $\alpha$ -diimine-Ni(II) catalysts even at elevated temperatures. Herein we report EPR spectroscopic study of Ni(I) species formed in the  $\text{LNiBr}_2/\text{MMAO}/\text{C}_2\text{H}_4$  catalyst system and discuss their possible role in ethylene polymerization.

## 2. Experimental

All samples for NMR and EPR spectroscopy were prepared in inert atmosphere using an Ar-filled glovebox. Complex **1** was synthesized as described [30]. Toluene, toluene- $d_8$ , 1,2-difluorobenzene were purchased from Aldrich and dried prior to use. Modified methylalumoxane was purchased from AKZO Nobel (MMAO-3 in heptanes,  $[\text{Al}] = 1.1 \text{ M}$ ).

$^1\text{H}$  NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer at 400.130 MHz using 5 mm o.d. glass NMR tubes. The NMR shifts were internally referenced to tetramethylsilane, with positive values in the low-field direction. EPR spectra (77 K) were measured in 3 mm quartz tubes on a CMS 8400 EPR spectrometer at 9.4–9.5 GHz, modulation frequency 100 kHz, modulation amplitude 5 G. Measurements were conducted in a quartz finger Dewar filled with liquid nitrogen. A solution of  $\text{Cu}(\text{acac})_2$  ( $2 \cdot 10^{-3} \text{ M}$ ) in toluene/ $\text{CH}_2\text{Cl}_2$  (1:1) was used as a standard for quantitative EPR measurements.

Ethylene polymerization was performed in a 0.3 L steel reactor. Pre-catalyst (solution of **1** in  $\text{CH}_2\text{Cl}_2$  for run 1 and solution of **1**/MMAO in heptanes for run 2) was introduced into the reactor in a sealed glass ampoule. The reactor was evacuated at  $80^\circ\text{C}$ , cooled down to  $20^\circ\text{C}$  and then charged with the freshly prepared solution of the co-catalyst in heptane. After setting up the desired temperature ( $50^\circ\text{C}$ ) and ethylene pressure (5 bar), the reaction was started by breaking the ampoule with the pre-catalyst. During the polymerization, ethylene pressure, temperature and stirring speed were maintained constant. The experimental unit was equipped with an automatic computer-controlled system for the ethylene feed, maintaining the required pressure, recording the ethylene consumption and providing the kinetic curve output both in the form of a table and as a graph. Weight-average ( $M_w$ ) and number-average ( $M_n$ ) molecular weights, molecular weight distributions (MWD), and polydispersities ( $M_w/M_n$ ) were obtained by GPC measurements on a Waters-150 chromatograph at  $150^\circ\text{C}$ , with trichlorobenzene as solvent. The number of branches of the polyethylene was determined by  $^{13}\text{C}$  NMR spectroscopy.

## 3. Results and discussion

### 3.1. Reaction of **1** with MMAO

As it was previously shown [26], reaction of **1** (Fig. 1) with 20 eq. of MMAO at  $-20^\circ\text{C}$  leads to the formation of the diamagnetic square-planar cationic complex of Ni(II):  $[\text{LNi}^{\text{II}}\text{-}^t\text{Bu}]^+[\text{MeMMAO}]^-$  (complex **2**, Scheme 1).

According to quantitative NMR spectroscopic measurements, the concentration of complex **2** does not exceed 40% of the total Ni content in the system. Besides diamagnetic complex **2**, paramagnetic EPR-active complex **3** was observed in the **1**/MMAO system. The concentration of **3** corresponds to  $50 \pm 15\%$  of the total Ni content. The frozen-solution EPR spectrum of **3** (Fig. 1) is characteristic of Ni(I) species ( $d^9$ -configuration,  $S = 1/2$ ). The axial g-factor anisotropy ( $g_{\parallel} = 2.21$ ,  $g_{\perp} = 2.06$ ) points to the axial symmetry of the first coordination sphere of **3**. The perpendicular component of the EPR spectrum of **3** ( $g_{\perp} = 2.06$ ) displays partially resolved hyperfine splitting from two nitrogen atoms with  $A_{\perp} = 1.06 \text{ mT}$ . On

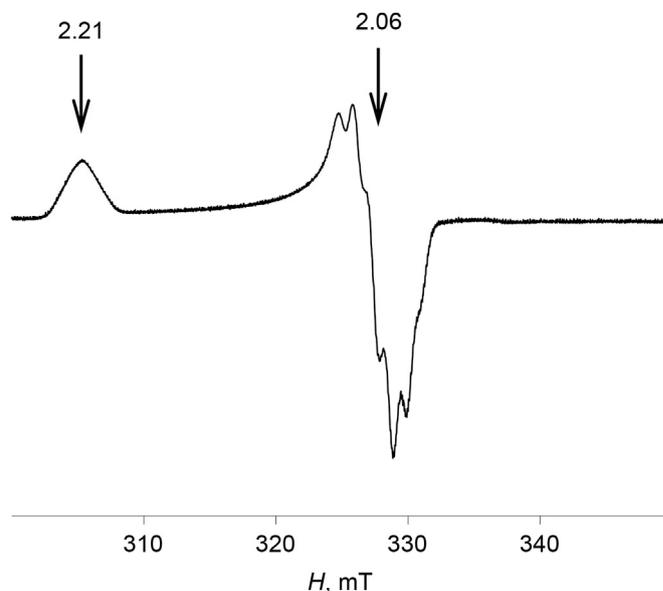
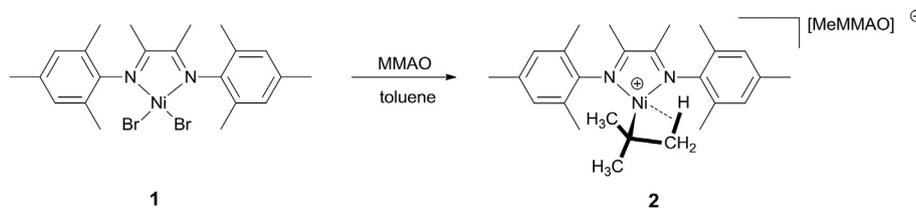


Fig. 1. EPR spectrum of **3** (77 K), obtained in system **1**/MMAO ( $[\mathbf{1}]/[\text{MMAO}] = 1/20$ , toluene/o-DFB (2/1),  $[\mathbf{1}] = 10^{-2} \text{ M}$ , mixed and stored 1 h at  $-20^\circ\text{C}$ ).

Scheme 1. Reaction of pre-catalyst **1** with MMAO.

the basis of these data, one can assume that  $\alpha$ -diimine ligand remains intact in the course of Ni(II)  $\rightarrow$  Ni(I) reduction. 5-Fold increase of the Al/Ni molar ratio (from [Al]/[Ni] = 20/1 to 100/1) gave rise to the growth of the Ni(I) content from 50 to 65%.

Two possible structures of **3** can be considered: cationic complex of Ni(I) with coordinated solvent molecule or molecules (S) ( $[\text{LNi}^{\text{I}}(\text{S})]^+[\text{MeMMAO}]^-$ ), and neutral Ni(I) complex with one alkyl ligand R ( $[\text{LNi}^{\text{I}}\text{R}]$ ). Taking into account a great excess of strongly Lewis acidic MMAO in the system, formation of the  $[\text{LNi}^{\text{I}}(\text{S})]^+[\text{MeMMAO}]^-$  species seems to be more realistic (Fig. 2). Moreover, an EPR spectrum identical to that of **3** is observed in the catalyst system **1**/MAO. Such identity well corresponds to the structures  $[\text{LNi}^{\text{I}}(\text{S})]^+[\text{MeMMAO}]^-$  and  $[\text{LNi}^{\text{I}}(\text{S})]^+[\text{MeMAO}]^-$ , exhibiting common cationic part. The assignment of **3** to the structure  $\text{LNi}^{\text{I}}(\mu\text{-Br})_2\text{AlMe}_2$ , by analogy with complex  $\text{L}_1\text{Ni}^{\text{I}}(\mu\text{-Br})_2\text{AlMe}_2$ , formed in the system  $\text{L}_1\text{NiBr}_2/\text{AlMe}_3$ , is less reasonable, because the EPR spectrum of  $\text{L}_1\text{Ni}^{\text{I}}(\mu\text{-Br})_2\text{AlMe}_2$  ( $g_1 = 2.361$ ,  $g_2 = 2.167$ ,  $g_3 = 2.052$  [27]) dramatically differs from that of **3** ( $g_{\parallel} = 2.21$ ,  $g_{\perp} = 2.06$ ).

Further warming the sample **1**/MMAO up to 25 °C leads to a rapid disappearance of the  $^1\text{H}$  NMR resonances of **2** and to simultaneous increase of the EPR signal of **3** (more than  $70 \pm 20\%$  of total Ni content). Besides the resonances of **3**, a less intense resonance of a new paramagnetic species **4** (**3**:**4** = 14:1) is observed in the EPR spectrum (Fig. 3a). The ratio **3**:**4** was the same for the samples with Al/Ni = 20 and Al/Ni = 500. It is worth mentioning that the Al/Ni ratio of 500 is typical for the real catalytic experiments. So, under the conditions mimicking those for practical polymerizations, a major part of Ni exists in the reaction solution in the form of the EPR active complex **3**.

The EPR spectrum of **4** displays the relatively narrow signal at  $g = 2.002$  with a 10-line hyperfine structure (Fig. 3a, insert). Schumann with co-workers have characterized aluminum complex with anion-radical of N,N- $\alpha$ -diimine ligand ( $\text{L}^{\bullet-}\text{AlMe}_2$ ), displaying EPR spectrum virtually identical to that of **4** [31]. Therefore, one can reasonably assume that **4** is  $\text{L}^{\bullet-}\text{AlMe}_2$  species (Fig. 2), a product of catalyst degradation via ligand scrambling. The mechanism of this degradation process is not clear at the moment.

### 3.2. Ethylene polymerization by the catalyst system **1**/MMAO

Catalyst **1** displays moderate activity toward ethylene

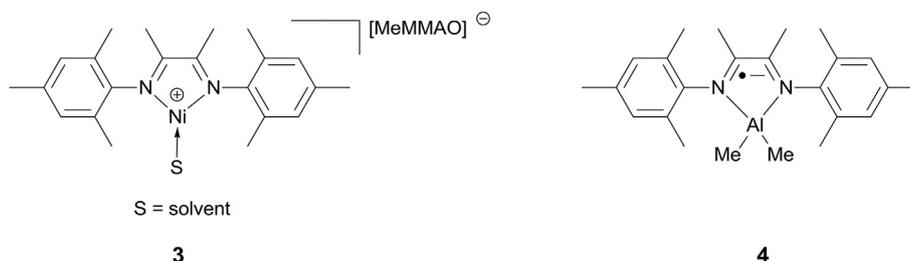
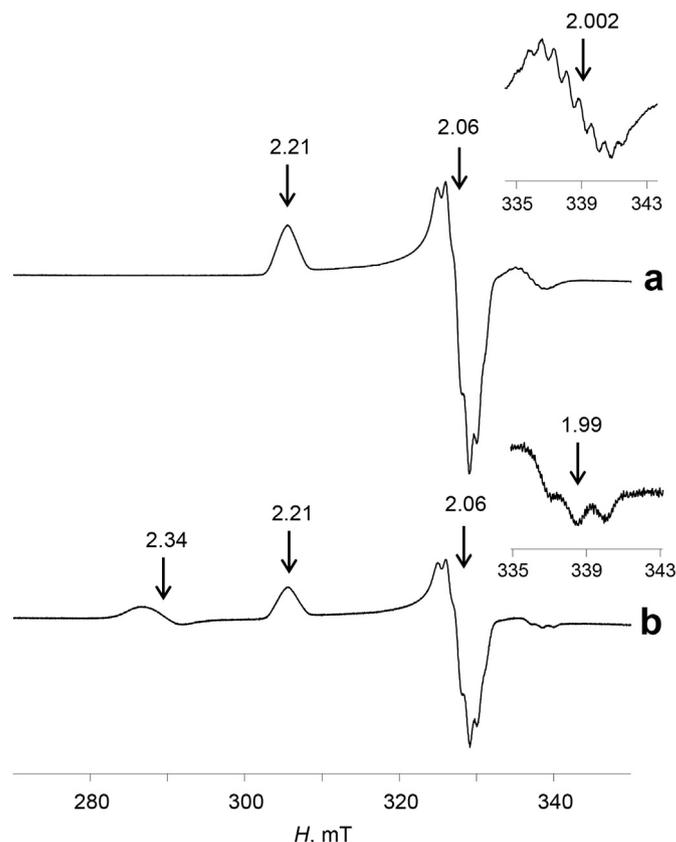
Fig. 2. Proposed structures of complexes **3** and **4**.

Fig. 3. EPR spectra (77 K) of the samples: (a) **1**/MMAO ([**1**]/[MMAO] = 1/20, toluene/*o*-DFB (2/1), [**1**] =  $10^{-2}$  M, mixed and stored 1 h at 25 °C); (b) after 600 eq. of ethylene addition to the sample (a) at  $-70$  °C.

polymerization at 50 °C, producing branched polyethylene with high molecular weight and narrow MWD (Table 1, run 1). The time profile of the ethylene polymerization rate by system **1**/MMAO exhibits high initial polymerization activity, followed by gradual decay (Fig. 4, run 1).

Taking into account the rapid and nearly complete reduction of

**Table 1**  
Ethylene polymerization data over the catalyst system 1/MMAO<sup>a</sup>.

run	PE yield, g	activity, kg <sub>PE</sub> ·mol <sub>Ni</sub> <sup>-1</sup> ·bar <sub>C<sub>2</sub>H<sub>4</sub></sub> <sup>-1</sup> ·min <sup>-1</sup>	M <sub>w</sub> , 10 <sup>3</sup> g/mol	M <sub>n</sub> , 10 <sup>3</sup> g/mol	M <sub>z</sub> , 10 <sup>3</sup> g/mol	M <sub>w</sub> /M <sub>n</sub>	M <sub>z</sub> /M <sub>w</sub>	Branches/1000C <sup>d</sup>
1 <sup>b</sup>	7.4	13.0	76	39	135	1.9	1.8	43
2 <sup>c</sup>	3.0	5.3	90	38	190	2.4	2.1	39

<sup>a</sup> Polymerization conditions: heptanes (100 cm<sup>3</sup>), T = 50 °C, P(C<sub>2</sub>H<sub>4</sub>) = 5 bar, n(Ni) = 1.9 μmol, [Al]/[Ni] = 500, time 1 h.

<sup>b</sup> A solution of pre-catalyst **2** in 0.5 ml of CH<sub>2</sub>Cl<sub>2</sub> was introduced in reactor.

<sup>c</sup> Complex **2** was mixed with 20 eq. of MMAO in heptanes, stored during 1 h at 25 °C, and then introduced in reactor.

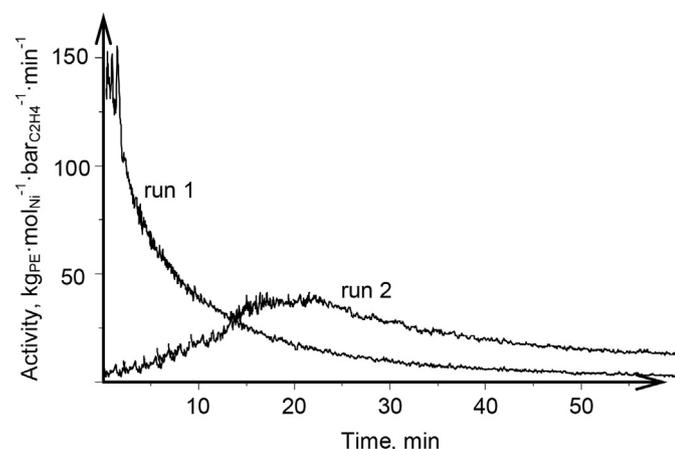
<sup>d</sup> Determined by <sup>13</sup>C NMR.

the cationic complex **2** into complex **3** in system 1/MMAO at room temperature, it is interesting to compare ethylene polymerization properties of two catalyst systems: the first one is 1/MMAO/C<sub>2</sub>H<sub>4</sub> system, in which the reagents were mixed simultaneously, the second one is the same system in which **1** was preliminary treated with MMAO, followed by ethylene addition. Rather unexpectedly, in spite of the virtually complete conversion of divalent complex **2** to monovalent complex **3** (more than 70 ± 20% of total Ni content), the second catalyst system is only two times less active than the first one, and produces PE with similar molecular-weight characteristics (compare runs 1 and 2, Table 1). At the same time, in contrast to run 1, the time profile of the polymerization rate for run 2 displays only negligible polymerization activity during the first 5 min of the reaction, then the activity gradually grows up and achieves maximum 20 min after the polymerization onset, followed by relatively slow decay (Fig. 4, run 2). These data are evidence that **3** participates in the catalytic process at least as a precursor of the active species of polymerization. Next, the effect of ethylene on the nature and concentration of various EPR active nickel species present in the catalyst system 1/MMAO/C<sub>2</sub>H<sub>4</sub> has been studied.

### 3.3. <sup>1</sup>H NMR and EPR studies of system 1/MMAO/C<sub>2</sub>H<sub>4</sub>

According to the <sup>1</sup>H NMR data, the addition of ethylene (200 eq.) to the sample 1/MMAO containing **2** at –20 °C leads to the immediate 5–10-fold drop of the intensities of the resonances of **2** and appearance of the broadened peaks of PE. After complete ethylene consumption, the <sup>1</sup>H resonances of **2** restore at least half of their initial intensities. The observed drop of the concentration of **2** in the presence of ethylene, accompanied by PE formation, is in agreement with the Brookhart's prediction of catalytic activity of such species in ethylene polymerization [14,15].

According to EPR data, the addition of ethylene (600 eq.) to the



**Fig. 4.** Time profiles of the ethylene polymerization rates by the catalyst system 1/MMAO.

sample 1/MMAO at –70 °C leads to a visible decrease of the intensity of resonances of **3**, and appearance of those of a new complex **5** ( $g_{\parallel} = 1.99$ ,  $N_{A\parallel} = 1.51$  mT,  $g_{\perp} = 2.34$ , Fig. 3b). In contrast to complex **3**, complex **5** exhibits hfs from one nitrogen atom. The relatively weak signal of **4** (if present) is masked by the  $g_{\parallel}$  component of the EPR spectrum of **5**. The concentration of **5** in the reaction mixture is strongly dependent on the amount of ethylene added ( $[3]/[5] = 15$  at  $n(\text{C}_2\text{H}_4)/n(\text{Ni}) = 200$ , and  $[3]/[5] = 4$  at  $n(\text{C}_2\text{H}_4)/n(\text{Ni}) = 600$ ). After complete ethylene consumption, **5** disappears, and initial concentration of **3** is restored.

The EPR spectra of **3** and **5** are significantly different. The EPR spectrum of **3** is typical for Ni(I) species with  $g_{\parallel} > g_{\perp}$  and displays hfs from two nitrogen atoms  $N_{A\perp} = 1.06$  mT. Complex **5** displays EPR spectrum with  $g_{\parallel} < g_{\perp}$  and hfs from one nitrogen atom  $N_{A\parallel} = 1.51$  mT. Probably, **5** is adduct of **3** with ethylene  $[\text{LNi}^{\text{I}}(\text{C}_2\text{H}_4)]^+[\text{MeMMAO}]^-$ . This assumption is supported by the ease of the reversible conversion between **3** and **5** upon the addition or consumption of ethylene. The dramatic difference between the EPR spectra of **3** and **5** can be caused by significant distortion of geometry of nickel(I) complex **3** upon ethylene coordination.

It is generally accepted that cationic alkyl complexes of Ni(II) are the active species of ethylene polymerization, catalyzed by  $\alpha$ -diimine complexes of nickel [24,25]. The data obtained here show that predominantly paramagnetic Ni(I) species are present in the catalyst system 1/MMAO/C<sub>2</sub>H<sub>4</sub> at room temperature (complexes **3** and **5**), whereas cationic alkyl complexes of Ni(II) (complex **2**) are not observed. Nevertheless, this system appears active in ethylene polymerization.

In principle, complex **5** can be the immediate precursor of the active species of polymerization, in spite of the absence of Ni-alkyl bond. Indeed, Gibson and coworkers have recently shown that the activation of bis(imino)pyridine cobalt(II) pre-catalyst by MAO leads to a bis(imino)pyridine cobalt(I) cationic species without cobalt-alkyl bond into which olefin insertion can occur. The authors proposed that the initiation of polymerization by this species involves incorporation of alkyl groups from the cocatalyst [38]. However, the similarity of the molecular characteristics of the polymers obtained in runs 1 and 2 of Table 1 apparently reflects the identity of the active species in these two systems. This can be the case if in the presence of ethylene, complexes **3** and **5** can convert back into the active Ni(II) species. We have not observed this conversion under the conditions of the NMR-tube experiment. Therefore, the exact role of Ni(I) species in ethylene polymerization, catalyzed by  $\alpha$ -diimine complexes of Ni(II), is still unclear and requires further studies.

## 4. Conclusions

Using <sup>1</sup>H NMR and EPR spectroscopy, the nickel species formed in the catalyst system 1/MMAO were studied (**1** = LNiBr<sub>2</sub>, L = 1,4-bis-2,4,6-dimethylphenyl-2,3-dimethyl-1,4-diazabuta-1,3-dien). It was shown that diamagnetic cationic complex  $[\text{LNi}^{\text{II}}\text{-tBu}]^+[\text{MeMMAO}]^-$  (**2**) is observed in system 1/MMAO only at low temperatures and rapidly decays at 25 °C to afford new EPR

active species **3** (major product) and **4** (minor product). **3**, the predominating form of nickel at room temperature, is nickel(I) complex with proposed structure  $[\text{LNi}^{\text{I}}(\text{S})]^+[\text{MeMMAO}]^-$ , S = solvent, while **4** is likely the product of catalyst degradation via ligand scrambling of the type  $\text{L}^{(\sigma-\pi)}\text{AlMe}_2$ . Upon the addition of ethylene to system **1**/MMAO/ $\text{C}_2\text{H}_4$ , complex **3** partially reversibly converts into the EPR active species **5**, which has been presumably assigned to the nickel(I) adduct  $[\text{LNi}^{\text{I}}(\text{C}_2\text{H}_4)]^+[\text{MeMMAO}]^-$ . After ethylene consumption, **3** restores its original concentration.

It is generally recognized that Ni(II) complexes (both neutral and cationic) play the key role in the ethylene polymerization process [24,25,32–37]. In the present work we have shown that reduction of nickel(II) centers to the monovalent state does not lead to the catalyst deactivation. The Ni(I) complex **3** formed in system **1**/MMAO is not an ultimate catalyst deactivation product but probably acts as a resting state of the catalyst. At the same time, the transformations of the Ni(I) species and their exact role in ethylene polymerization are unclear and will be addressed in future studies.

### Conflicts of interest

The authors declare no competing financial interest.

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